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(54) Title: POLYAMPHOLYTE COAGULANT IN THE PAPERMAKING PROCESS**(57) Abstract**

In the papermaking process, a polyampholyte coagulant is used as a retention/drainage/formation aid in a papermaking process; is used to treat coated broke where the white pitch or stickies and pigments are affixed to the long fibers and fiber fines; and is used to clarify the process water where the solids from the white water are either settled out or floated for their removal from the water. As a retention/drainage formation aid, the polyampholyte coagulant polymer is added to the papermaking cellulosic slurry prior to the first or after the last shearing stage, and, optionally, a flocculant may be added either before the addition of the polyampholyte coagulant or before the first or the last shearing stage. The polyampholyte coagulant has a weight average molecular weight from 10 thousand to 20 million, is in emulsion or solution form, and may comprise a copolymer of acrylic acid (anionic) and diallyl dimethyl ammonium chloride (cationic) in a weight percentage ratio range of from about 1:999 to about 99:1 based on the dry weight of the polyampholyte, or may comprise a terpolymer of acrylamide (nonionic), acrylic acid (anionic), and diallyl dimethyl ammonium chloride (cationic).

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POLYAMPHOLYTE COAGULANT IN THE PAPERMAKING PROCESS

This patent application claims priority based on
Provisional Application Serial No. 60/111,679 filed
5 December 10, 1998.

BACKGROUND OF THE INVENTION1. Field Of The Invention

10 The present invention relates to the use of polyampholyte coagulant polymers in several areas of the papermaking process: 1) as a retention/drainage/formation aid; 2) to treat coated broke where the white pitch or stickies and pigments are affixed to the long fibers and
15 fiber fines; and 3) in process water clarification to settle or float the solids from the white water for removal of the solids from the water.

2. Description Of The Background Art

20 In the production of paper or paperboard, a dilute aqueous composition known as "furnish" or "stock" is sprayed onto a moving mesh known as a "wire". Solid components of this composition, such as cellulosic fibers, fines, and inorganic particulate mineral fillers
25 are drained or filtered by the wire to form a paper sheet. The percentage of solid material retained on the wire is known as the "first pass retention" of the papermaking process.

30 Retention is believed to be a function of different mechanisms, such as filtration by mechanical entrainment, electrostatic attraction, and bridging between the fibers and the fillers in the furnish. Because both the cellulosic fibers and many common filler materials are negatively charged, they are mutually repellent.
35 Generally, the only factor tending to enhance retention is mechanical entrainment. Therefore, a retention aid is

generally used to improve retention of the fibers and fillers on the wire.

Drainage relates to the rate of removal of water from the furnish as the paper sheet is formed. Drainage usually refers to only water removal which takes place in the "drainage zone" (gravity and vacuum sections) of the Fourdrinier or twin wire paper machine primarily before any pressing of the wet paper web subsequent to formation of the web. Thus, drainage aids are used to improve the overall efficiency of dewatering in the production of paper or paperboard.

Formation relates to the uniformity of the paper or paperboard sheet produced from the papermaking process. Formation is generally evaluated by the variance of light transmission through a paper sheet. A high variance is indicative of "poor" formation and low variance is generally indicative of "good" formation. Generally, as the retention level increases, the level of formation generally decreases from good formation to poor formation.

It can be appreciated that improvements in retention, drainage and formation properties of the final paper or paperboard sheet are particularly desirable for several reasons, the most significant of which is productivity. Good retention and good drainage enable a paper machine to run faster and to increase production. Good sheet formation improves sheet quality. These improvements are realized by the use of retention and drainage aids. These retention and drainage aids are generally added to the furnish as the furnish approaches the headbox of the paper machine and may comprise a coagulant/flocculant system used in conjunction with one or more shearing stages.

Generally, the coagulant is a low molecular weight cationic synthetic polymer that reduces the negative surface charges on the fiber, fines, and/or filler particles to accomplish a degree of agglomeration of such particles. The flocculant, which generally is a high molecular weight cationic, nonionic, or anionic synthetic polymer, bridges the particles and/or agglomerates, from one surface to another, thereby binding the particles into larger flocs. The larger flocs increase retention of the particles; however, as they are filtered out of the water onto the fiber web, the pores of the flocs are covered, thereby reducing the drainage efficiency of the fiber web. The larger flocs can be broken down by shearing which is provided by one or more of the cleaning, mixing and pumping stages of the papermaking process.

Greater retention of fines and fillers permits a reduction in the content of cellulosic fiber. As pulps of less quality are employed to reduce papermaking costs, the retention aspect of papermaking becomes even more important. This is due to the generally greater level of fines found in lower quality pulps, such as recycled fiber and coated broke.

Greater retention of fines, fillers, and other slurry components reduces the amount of such substances lost to the white water. This reduces the amount of material wastes, the cost of waste disposal, and the adverse environmental effects therefrom.

There is a need in the art to provide an improved coagulant/flocculant system which replaces the cationic coagulant/high molecular weight anionic flocculant system of the prior art resulting in a substantial improvement of the retention and drainage properties of the paper furnish and the physical properties of the formed paper

product such as formation and brightness. This may be particularly true for paper furnishes containing recycled deinked fiber, groundwood, bleached fiber linerboard and/or coated broke and either treated or untreated fillers.

5 Coated broke may be used a portion of the furnish in certain grades of paper. Coated broke is the name given to coated paper which has been repulped. The coated paper generally contains natural or synthetic pigments, binders, dispersants, water and other agents. The natural pigments may be titanium dioxide, clay, talc, or calcium carbonate. The binders act to adhere the pigment particles to each other and to the fiber and fines in the paper web. Generally, the primary components of the 10 coated broke are pigments and binders. During repulping, the binders such as starch, polyvinyl acetate (PVA), latex, styrene butadiene rubber (SBR), polyvinyl alcohol (PVOH), and other synthetic organic binders, are 15 liberated from the coating. Untreated, the binders (latex, SBR, PVA, and PVOH) can agglomerate at shear points or precipitate out of solution due to pH or 20 temperature shock in the furnish, depositing on tank walls, wires, boil blades, rolls, felts, dryer cans, or piping shear points. These deposits can break loose 25 causing defects or breaks in the paper web. The deposition of binder agglomerates at the shear points is referred to as "white pitch" or "stickies".

30 There is a further need to prevent the "white pitch" or "stickies" of the coated broke from forming and depositing in the sheet which can result in defects and/or breaks in the paper web.

The white water (process water) in the paper machine is generally piped to tanks for recycling purposes, which is referred to as a "saveall". Several methods or types

of equipment can be used for removal of the solids and/or additives from this white water in the saveall so that the water can be recycled and returned in the papermaking process in as pure a form as possible.

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There is a further need to provide an improved method for recovering the solids, i.e., fibers and fillers, from the white water in the saveall of a paper machine.

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SUMMARY OF THE INVENTION

The invention has met these needs. In a first aspect of the invention, a polyampholyte coagulant is used in the papermaking process to improve retention of pigments and fiber fines and/or to improve drainage and formation of the sheet being formed. Optionally, a water soluble flocculant polymer is used with this polyampholyte coagulant.

15

The paper may be produced by forming an aqueous cellulosic slurry comprising recycled deinked newsprint, bleached or unbleached chemical pulps (hardwood or softwood), pulp fibers, recycled fiber (bleached or unbleached), coated broke, and ground or mechanical pulp which may or may not contain a mineral filler or pigment; adding the suspension through one or more shear stages; 20 driving the suspension to form a wet web; pressing and drying the wet web to produce the final sheet. The polyampholyte coagulant, preferably, is added to the slurry prior to the first or after the last shearing stage, and the flocculant may be added either before the addition of the coagulant or before the first or after the last shearing stage before the headbox. The polyampholyte coagulant may also be added after the flocculant or can be combined with the flocculant and added to the aqueous cellulosic slurry ahead of the

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headbox. The polyampholyte may be added to the aqueous cellulose slurry without the flocculant. The polyampholyte coagulant may be supplied as a true solution in water, or as an emulsion where it is 5 dispersed in a carrier oil, and is dissolved in water and added as a dilute aqueous solution to the furnish slurry during the papermaking process.

In a second aspect of the invention, a polyampholyte polymer is used to treat coated broke prior to or after 10 the coated broke is added to the paper furnish. After the coated paper is repulped, the polyampholyte polymer is added to the coated broke in order to attach the "white pitch" and the pigments to the longer fibers, thereby lessening the amount of "white pitch" being 15 deposited onto sites throughout the papermaking process. This treated coated broke can then be used as pulp in a papermaking process where a polyampholyte polymer may be used as a retention/drainage/formation aid in accordance with the teachings of a first aspect of the invention.

In a third aspect of the invention, a polyampholyte polymer is used in saveall applications whereby the 20 polyampholyte polymer is added to the white water to cause the fiber and filler to settle out of the water or to float in air flotation type savealls for their easy 25 removal therefrom. The clarified water can then be reused.

The polyampholyte polymer has a molecular weight ranging from about 10 thousand to 20 million. The 30 polyampholyte polymer may comprise two, three or more monomers with a total ratio of a:b ranging from about 1:99 to 99:1 where a) is the anionic monomer and (b) is the cationic monomer. The weight percent ratio of these monomers in a polymer containing two or more monomers (a:b:c) may range from about 1:1:98 to 1:98:1 or 98:1:1

where a) is the nonionic monomer, b) is the anionic monomer and c) is the cationic monomer based on the dry weight of the polyampholyte.

5 If a flocculant is used with the polyampholyte coagulant as a retention/drainage/formation system, preferably the flocculant is a high molecular weight anionic, nonionic, or cationic polymer with a molecular average molecular weight ranging from about 1 million to about 30 million.

10 The preferred dosage for the coagulant may range from about 0.0025% to about 3.0%, and more preferably, from about 0.005% to about 1.5%, based on the dry weight of the solids. The preferred dosage for the flocculant would range from about 0.0025% to about 3.0%, and more 15 preferably from about 0.005% to about 1.5%, based on the dry weight of the solids in the furnish.

BRIEF DESCRIPTION OF THE INVENTION

20 Figure 1 is a graph illustrating press solids (%) and brightness results for certain copolymer coagulants and cationic coagulants and includes a terpolymer polyampholyte of the invention (Product B) in a fine paper furnish.

25 Figures 2 - 4 are graphs illustrating brightness results for certain copolymer coagulants and cationic coagulants and includes several polyampholytes (terpolymers and copolymers) of the invention in a newsprint or super calendered (SC) grade furnish.

DETAILED DESCRIPTION OF THE INVENTION

30 As used herein, the term "paper" includes products comprising a cellulosic sheet material including paper sheet, paperboard, and the like.

The term "polyampholyte" is any polymer comprising at least a cationic charge and an anionic charge and can include a copolymer, a terpolymer, or a polymer containing three or more monomers.

5 A first aspect of the invention pertains to the use of a polyampholyte coagulant polymer and, optionally, a high molecular weight flocculant as a retention/drainage/formation aid for particular use in the wet end of a paper machine in the papermaking process
10 for both acid, neutral, and alkaline paper grades.

15 The components of the coagulant/flocculant system of the invention may be added simultaneously or sequentially to the furnish at the same or different points of addition but, preferably, are added in the manner and
order described hereinbelow.

20 A conventional papermaking process contains one or several shearing stages, i.e., mixing and cleaning of the furnish or stock as it passes from the stock preparation area through the papermaking process. Thick stock generally comprises filler, fiber, strengthening agent and/or other additives and water. The thick stock
25 generally is diluted with white water to form "thin stock" by passing the thick stock and dilution water through a mixing pump. The stock can be cleaned by passing it through vortex cleaners or a centri-screen and/or it may be pumped to the paper machine by one or more centrifugal pumps (transfer or fan pumps). The thin stock may be pumped to centrifugal cleaners by a first
30 fan pump. The thin stock may be cleaned further by passing it through a centriscreen or pressure screen prior to it being passed into a headbox in preparation for the sheet forming process.

In the first aspect of the invention, preferably, the polyampholyte coagulant polymer is added to the thin stock before the fan pump or after the centriscreen and the flocculant is added to the thin stock either as the
5 thin stock exits the fan pump or prior to the thin stock being passed through the centriscreen before, after, or simultaneously with the addition of the polyampholyte coagulant polymer.

In the invention, the polyampholyte coagulant is any
10 polymer comprising at least a cationic charge and an anionic charge. This polyampholyte may be a copolymer having anionic and cationic monomers or a terpolymer having nonionic, anionic and cationic monomers. This polyampholyte may also comprise more than three monomers
15 which could be one or more anionic, cationic, and/or nonionic monomers.

In the instance where the polyampholyte coagulant is a copolymer derived from anionic and cationic monomers, the anionic monomer may be selected from the group
20 consisting of acrylic acid, methacrylic acid, 2-acrylamido-2-methylpropane sulfonic acid, sodium vinyl sulfonate, itaconic acid, 2-acrylamido-2-methylbutanoic acid and acrylamidoglycolic acid or their corresponding salts. The acrylic acid and the methacrylic acid may be
25 introduced into the polyampholyte polymer by hydrolysis of acrylamide and methacrylamide, respectively. The cationic monomer may be selected from the group consisting of diallyl dimethyl ammonium chloride, (DADMAC), acryloyloxyethyl trimethyl ammonium chloride
30 (AETAC), methacryloyloxyethyl trimethyl ammonium chloride, acrylamidopropyl trimethylammonium chloride, and methacrylamido propyl trimethyl ammonium chloride.

In the instance where the polyampholyte consists of two or more monomers derived from nonionic, anionic, and cationic monomers, the anionic monomer may be selected from the group consisting of acrylic acid (AA) or its homologues, sodium acrylate, vinyl sulfonic acid, methacrylic acid, 2-acrylamido-2-methylpropane sulfonic acid (AMPS), sodium vinyl sulfonate, itaconic acid, sodium itaconate, acrylamidoglycolic acid, 2-acrylamido-2-methyl butanoic acid, 2-acrylamido-2-methyl propane phosphonic acid, sodium salt, sodium vinyl phosphonate, allyl phosphonic acid, and/or mixtures thereof. The acrylic acid and the methacrylic acid may be introduced into the terpolymer by hydrolysis of acrylamide and methacrylamide, respectively, or the acrylic acid may be introduced into the terpolymer by adding acrylic acid prior to polymerization. The cationic monomer may be selected from the group consisting of diallyl dimethyl ammonium chloride (DADMAC), dialkyl diallyl ammonium monomer, quarternary dialkyl diallyl ammonium, methacryloxyethyl trimethyl ammonium chloride, acrylamido propyl trimethyl ammonium chloride, acryloyloxyethyl trimethyl ammonium chloride (AETAC), methacrylamido propyl trimethyl ammonium chloride, quaternized derivatives of N,N-dimethyl amino ethyl methacrylate, dimethyl amino ethyl acrylate, and dibutyl amino ethyl methacrylate. The nonionic monomer may be selected from the group consisting of acrylamide (AM), N-vinylamide, N-alkylacrylamide, vinyl acetate, acrylate esters, diacetone acrylamide, and N, N-dialkylacrylamide, vinyl pyrrolidone, and vinyl alcohol.

The copolymer polyampholyte of the invention has a weight percent ratio, i.e., a) anionic monomer to b) cationic monomer, ranging from about 1:99 to about 99:1,

and preferably, 2:98 to 98:2 for monomers a:b, and has a molecular weight in excess of about 50,000.

The weight percent ratio of the terpolymer polyampholyte of the invention, i.e., a) nonionic moiety to b) anionic monomer to c) cationic monomer, ranges from about 1:1:98 to about 1:98:1 to about 98:1:1, preferably, about 18:2:80 to about 25:50:25, and most preferably about 48:2:50 to about 25:25:50, or about 41:13:46 for monomers a:b:c. The molecular weight is less than about 10 \times 10⁶. Preferred terpolymer compositions are: 1) acrylamide/acrylic acid/diallyl dimethyl ammonium chloride (AM/AA/DADMAC) in the weight ratio range of 48:2:50 to 25:25:50, and 2) AM/AMPS/DADMAC (acrylamide/2-acrylamido-2-methyl propane sulfonic acid/diallyl dimethyl ammonium chloride) in a weight ratio 41:13:46.

Preferably, the nonionic moiety of the terpolymer polyampholyte has a molecular weight of about 5 \times 10⁵ and preferably less than 10 \times 10⁶, i.e., about 7 \times 10⁶.

It is theorized that the cationic moiety of the polyampholyte coagulant draws the negatively charged pulp fines and fillers into small uniformly spaced agglomerates. The anionic charge helps maintain the uniform spacing, thus enhancing brightness through a good distribution of the filler in the paper web. The molecular weight and charge of the amphotolyte enhances drainage by uniform spacing of the agglomerates which allows the water to pass between the agglomerates, but which does not create large openings or void spaces which would give "good" free drainage but result in "poor" vacuum drainage. The high molecular weight polymer of the invention comprises an agent for aggregating the fines and fibers in the papermaking furnish, thereby giving better drainage and retention.

An effective amount of a polyampholyte coagulant/flocculant system of the invention should be employed. The effective amount for a given cellulosic furnish being treated generally depends on the source and type of pulp, the water chemistry, and the amount of pulp fines and fillers. Preferably, the effective coagulant dosage will be in an amount of at least about 0.01 (active) pounds per ton (0.0005% by weight) based on the dry weight of the solids in the aqueous cellulosic furnish. The effective amount of flocculant dosage will be an amount of at least about 0.01 (active) pounds per ton (0.0005% by weight) of dry solids in the aqueous cellulosic furnish.

Preferably, the dosage of the coagulant is about 0.01 (active) pounds per ton, or about 0.0005 weight % to about 3 weight % of the total weight of the dry weight of solids in the aqueous cellulosic furnish and, most preferably, 0.005 weight % to 1.5 weight %. The dosage of the flocculant ranges from about 0.05 to about 30.0 (active) pounds per ton based on the dry weight of the solids in the aqueous cellulosic furnish, or 0.0025 weight % to 1.5 weight % of the total weight of the dry solids, and, preferably, 0.0025 weight % to 1.0 weight %.

The coagulant/flocculant system of the invention can generally be successfully added to aqueous cellulosic furnishes over the entire pH range customarily employed in the papermaking process. Preferably, the coagulant/flocculant system of the invention is added to aqueous cellulosic furnishes having a pH from about 3 to 10. Therefore, it will be appreciated by those skilled in the art that the system of the invention may be added to paper furnishes that are acid, alkaline, or neutral in character. Where generally an acid furnish has a pH range from about 3.8 to 6.5, an alkaline furnish has a pH

range of about 7.2 to greater than about 10, and a neutral furnish has a pH range of from about 6.5 to 7.2.

As stated hereinabove, preferably, the polyampholyte coagulant polymer of the invention is added to the paper furnish before the final shearing stage and the high molecular weight flocculant polymer is added before or after the coagulant and, which may or may not be before the last shearing stage so "good mixing" of the polymers occurs before the thin stock enters the headbox of the paper machine.

Examples of high molecular weight polymer flocculants suitable for use herein are those having a weight average molecular weight of about 100,000 or more, especially 500,000 or more. Preferably, the molecular weight is about 1 million and often above about 5 million, for instance in the range 10 to 30 million or more. These polymers may be linear, branched, cationic, anionic, nonionic, amphoteric, or hydrophobically modified polymers of acrylamide or other nonionic monomers.

If a cationic flocculant polymer is used, the polymer may contain at least one cationic monomer selected from the group of a quaternary dialkydiallyl ammonium, methacryloyloxyethyl trimethyl ammonium chloride, methacryloyloxyethyl trimethyl ammonium methosulfate, acrylamido propyl triethyl ammonium chloride, methacrylamido propyl triethyl ammonium chloride, acryloyloxethyl trimethyl ammonium chloride, quaternized derivatives of N, N-dimethyl amino ethyl methacrylate, dimethyl amino ethyl acrylate, diethyl amino ethyl acrylate, dibutyl amino ethyl methacrylate, dimethyl amino methyl acrylate, demethyl amino methyl methacrylate, diethyl amino propyl acrylate, diethyl amino propyl methacrylate, ammonium methosulfate, amino

methylated polyacrylamide and combinations thereof. As used herein, the term "dialkyldiallyl ammonium monomer" refers to any water soluble monomer of the formula [DADAAX], which represents dialkyldiallyl ammonium X, 5 wherein each alkyl group is independently selected from an alkyl group of form about 1 to 18 carbon atoms, and preferably from about 1 to 4 carbon atoms, and wherein X is any suitable counterion. Preferably, the counterions are selected from the group consisting of conjugate bases 10 of acids having an ionization greater than 10^{-3} , and more preferably selected from the group consisting of a halide, hydroxide, nitrate, acetate, hydrogen sulfate, methyl sulfate, and primary phosphate. The halide may be any halide, and more preferably is selected from the 15 group consisting of fluoride, bromide and chloride. Preferably, the quaternary dialkyldiallyl ammonium halide monomer is selected from the group consisting of dimethyl 20 diallyl ammonium chloride, diethyl diallyl ammonium chloride, dimethyl diallyl ammonium bromide, and diethyl diallyl ammonium bromide.

Also, the cationic flocculant polymer may contain at least one anionic monomer selected from the group of 25 acrylic acid, methacrylic acid, 2-acrylamido-2-methylpropanesulfonic acid, crotonic acid, sodium vinyl sulfonate, acrylamidoglycolic acid, 2-acrylamido-2-methylbutanoic acid, 2-acrylamido-2-methylpropanephosphonic acid, sodium vinyl phosphonate, allyl phosphonic acid. Derivatives of the above anionic monomers are well known and those are useful in the 30 present invention. The polymer may contain nonionic portions and may contain at least one nonionic monomer from the group of N-vinylamide, N-alkylacrylamide, vinyl acetate, vinyl alcohol, acrylate esters, diacetone acrylamide, N, N-dimethyl acrylamide.

The cationic flocculant polymer may have a weight average molecular weight ranging from about 500,000 to about 20 million.

If an anionic high molecular weight water soluble 5 flocculant polymer is used, the polymer is derived from monomers from the group of acrylic acid or its homologues, sodium acrylate, vinyl sulfonic acid, sodium vinyl sulfonate, itaconic acid, sodium itaconate, 2-acrylamido-2-methylpropanesulfonic acid sodium salt, 10 acrylamidoglycolic acid, 2-acrylamido-2-methylbutanoic acid, 2-acrylamido-2-methylpropanephosphonic acid, sodium vinyl phosphonate, allyl phosphonic acid and/or admixtures thereof. It may also be either hydrolyzed acrylamide polymers or copolymers of its homologues, such 15 as methacrylamide. The polymer may contain nonionic portions and may contain at least one nonionic monomer from the group of acrylamide, N-vinylamide, N-alkylacrylamide, vinyl acetate, vinyl alcohol, acrylate esters, diacetone acrylamide, N, N-dialkylacrylamide. 20 Acrylic acid and methacrylic acid may conveniently be introduced into the polymer by hydrolysis of acrylamide and methacrylamide, respectively. The anionic polymer may be homopolymers, copolymers, or terpolymer. The most preferred high molecular weight homopolymer is 25 polyacrylic acid or its salts. The most preferred high molecular weight copolymers are acrylic acid/acrylamide copolymer; and sulfonate containing polymers such as 2-acrylamido-2-methylpropane sulfonate/acrylamide; acrylamido methane sulfonate/acrylamide; 2-acrylamido 30 ethane sulfonate/acrylamide; 2-hydroxy-3-acrylamide propane sulfonate/acrylamide. The most preferred high molecular weight terpolymers are acrylic acid/acrylamide/2-acrylamido-2-methylpropane sulfonate; acrylic acid/acrylamide/acrylamido methane sulfonate;

acrylic acid/acrylamide/2acrylamido ethane sulfonate; acrylic acid/acrylamide/2-hydroxy-3-acrylamide propane sulfonate. Commonly accepted counter ions may be used for the salts such as sodium ion, potassium ion, etc.

5 The anionic flocculant polymer may have a weight average molecular weight ranging from about 1 million to about 30 million.

10 If the high molecular weight flocculant is comprised of a nonionic polymer, preferably it would be a polyacrylamide having a weight average molecular weight of about 500,000 to about 20 million.

15 Preferably, the polyampholyte coagulant polymer consists of three or more monomers comprising nonionic, anionic and cationic monomers which preferably in emulsion form or solution form has a weight % ratio based on the total dry weight of the polyampholyte coagulant ranging from 48:2:50 to 25:25:50 for AM/AA/DADMAC and AM/AMP/DADMAC having a weight ratio of about 41:13:46. In emulsion form, the polyampholyte coagulant is about 20 25-50% active, and in solution form, the polyampholyte coagulant is about 4-20% active.

25 The initial thick stock can be made from any conventional papermaking stock such as traditional chemical pulps, for instance bleached and unbleached sulphate or sulphite pulp, mechanical pulps, such as groundwood, thermochemical or chemi-thermochemical pulp, or recycled pulp such as deinked waste fiber filler composites, including coated broke and broke from aggregating or recycling processes and any mixtures 30 thereof.

The furnish employed in the final paper can be substantially unfilled, e.g., containing less than 10% and generally less than 5% by weight filler in the final paper, or the filler can be provided in an amount of up

to 50% based on the dry weight of the solids of the stock or up to 40% based on the dry weight of the paper. When 5 filler is used, any conventional white pigment filler, such as calcium carbonate, kaolin clay, calcined kaolin, titanium dioxide, chalk or talc or a combination thereof may be present. The filler is preferably incorporated into the stock in a conventional manner, prior to the addition of the coagulant/flocculant system of the invention. If the furnish is neutral, i.e., a pH range 10 from about 6.5 to 7.2, such as that used in newsprint, lightweight coated or super-calendared grades, an acid 15 resistant calcium carbonate filler of the prior art could be used such as that discussed in U.S. Patent Nos. 5,101,489; 5,599,388; 5,647,902; 5,685,900; and 5,711,799 which are owned by the same assignee of the present 20 invention. For example, U.S. Patent No. 5,711,799 discloses a calcium carbonate treated with sodium aluminate in order to make the carbonate acid resistant 25 to the acidic pulp.

The furnish employed in the invention may include 20 known optional additives, such as rosin, alum, 25 sizing agents, optical brightening agents, or a 30 strengthening or binding agent which for example may comprise a starch, often a cationic starch or a guar gum.

The amounts of fiber, filler or pigment, and other 25 additives such as strengthening agents or alum can all be 30 conventional. Typically, the thin stock has a solids content from 0.1% to 1.5% by weight which consists mostly 35 of fiber.

The total amount of the water soluble polyampholyte 30 coagulant polymer in the furnish may be in the range of about 0.0005 to 3.0 weight %, and more preferably in the range of about 0.005 weight % to about 1.5 weight % (dry weight based on the dry weight of the solids in the stock

or furnish). The total amount of the water soluble high molecular weight flocculant polymer in the furnish may be in the range of about 0.0025 to 3.0 weight %, and more preferably, in the range of about 0.0025 weight % to 5 about 1.5 weight % (dry weight based on the dry weight of the solids in the stock or furnish).

The inventors have found that a low molecular weight polyampholyte coagulant, which may be a copolymer or 10 three (terpolymer) or more monomers when used in conjunction with a high molecular weight flocculant polymer can increase drainage and retention in the papermaking process and improve sheet formation and brightness characteristics of the paper.

In the following examples, the following polymers 15 were used:

A:	A terpolymer in a solution which is 8.0% active formed of 25% by weight acrylamide (AM); 25% by weight acrylic acid; and 50% by weight diallyl dimethyl ammonium chloride (DADMAC).
B:	A terpolymer in emulsion form which is 30.5% active formed of 45% by weight acrylamide; 5% by weight acrylic acid; and 50% by weight of DADMAC, and having an intrinsic viscosity (IV) of about 5.0. (4-5 MM MW)
C:	A terpolymer in a solution which is 8.0% active formed of 50% by weight acrylamide; 5% by weight acrylic acid; and 50% by weight DADMAC, where 5% of the acrylamide is post hydrolyzed to acrylic acid.
D:	A copolymer in a 8.0% active solution formed of 50% by weight AM and 50% by weight DADMAC. (4-5 MM MW)
E:	A copolymer being 30.6% active in emulsion form and formed of 50% by weight AM and 50% by weight DADMAC. (4-5 MM MW)
F:	A copolymer being 40.0% active in emulsion form and formed of 25% by weight AM and 75% by weight DADMAC. (4-5 MM MW)
G:	A copolymer being 8.4% active in solution form and formed of 50% by weight AM and 50% by weight DADMAC. (4-5 MM MW)

H:	Modifoed Polyethyleneimine (Polyamin SKA® B.A.S.F.) (~ 1-2 MM MW)
I:	Low molecular weight copolymer being 20% active in solution and formed of 50% by weight AM and 50% by weight DADMAC. (4-5 MM MW)
J:	Low molecular weight polyDADMAC 20% active solution polymer (1-2 MM MW).
K:	Low molecular weight polymer formed of 100% by weight polyamine (1-2 MM MW).
L:	A high charge, high molecular weight cationic flocculant copolymer of 77/23 AM/AETAC in emulsion form. (MW~ 10-15 MM)
M:	A high molecular weight 40% active flocculant copolymer of 70 wt % AM/30 wt % AETAC.
N:	A low molecular weight polyDADMAC formed of (< 1-2 MM MW) Being 40% active.
O:	Copolymer formed of 50% by weight AM and 50% by weight DADMAC. Being 36% active.
P:	Polymer formed of Saponite - a trioctahedral clay mineral having aluminum substitution in central octahedral layer and in the outer tetrahedral layers.
R:	Aminomethylene polyacrylamide 7% active solution polymer.
S:	High molecular weight polymer flocculant formed of 77% weight % AM & 23 weight % AETAC (10-15 MM MW)
T:	High molecular weight polymer flocculant formed of 40% AM & 60% AETAC (10-15 MM MW)
U:	High molecular weight polymer flocculant formed of 36% AM & 70% AETAC (10-15 MM MW)
V:	20:1 wt/wt blend of (polyvinyl aluminum chloride) PAC/DADMAC 30% active solution polymer (10-100 M MW).
W:	Coagulant 10/1 wt/wt active PAC/Polyamine Blend (1-2 MM MW) 28% active
X:	Coagulant formed of 80% by weight DADMAC & 20% by weight AA blend
Y:	Coagulant formed of 70 weight % AM & 30% DADMAC solution polymer 4.0% active (4-5 MM MW)
Z:	A nonionic flocculant formed of AM (10-15 MM MW)

A1:	A low charge anionic flocculant formed of 95% weight % AM & 5 weight % hydrolyzed AM (10-15 MM MW)
B1:	A high charge cationic flocculant formed of 97 weight % AM & 3 weight % AETAC (10-15 MM MW)
C1:	A high charge anionic flocculant formed of 100% AM of which 30% is post hydrolyzed (10-15 MM MW)
D1:	Water washed clay
E1:	Coagulant formed of 33% active polyaluminum chloride sulfate
G1:	Coagulant formed of 50 weight % AM & 50 weight % DADMAC post hydrolyzed 50% (4-5 MM MW)
H1:	Coagulant formed of AM/AMPS/DADMAC (4-5 MM MW) in weight ratio 41:13.2:45.7.
I1:	Cationic flocculant formed of 15 weight % AETAC & 85 weight % AM (10-15 MM MW)
J1:	Cationic flocculant formed of 90 weight % AM & 10 weight % AETAC (10-15 MM MW)
F1:	Calcined clay
L1:	23/77 AETAC/AM cationic flocculant (10-15 MM MW)
M1:	Polyamine 50% active solution (~500,000 MM MW)
N1:	Medium molecular weight polyDADMAC 40% active solution polymer (1-2 MM MW).
O1:	A copolymer being 42.0% active in emulsion form and formed of 50% by weight AM and 50% by weight DADMAC. (4-5 MM MW)
P1:	A terpolymer being 30.5 % active in emulsion form and formed of 17.5% by weight of AM, 2.5% by weight AA and 50 % by weight of DADMAC.
Q1:	A terpolymer being 30.5 % active in emulsion form and formed of 47.5% by weight of AM, 2.1% by weight AA and 50 % by weight of DADMAC.
R1:	A terpolymer being 30.5 % active in emulsion form and formed of 47.5% by weight of AM, 2.1% by weight AA and 50 % by weight of DADMAC.
S1:	A terpolymer being 8.0 % active in solution form and formed of 38% by weight of AM, 17% by weight AA and 45 % by weight of DADMAC.

T1	A terpolymer being 20.0 % active in solution form and formed of 46% by weight of MAPTAC, 46 % by weight AA and 8 % by weight of DADMAC.
U1	A terpolymer being 10.0 % active in solution form and formed of 60 mole % of VP, 30 mole % AMPS and 10 mole % of AM.
V1	A terpolymer being 10.0 % active in solution form and formed of 60 mole % of NN-dimethylacrylamide, 30 mole % AMPS and 10 mole % of AM.
W1	A terpolymer being 7.2 % active in solution form and formed of 70 mole % of AM, 15 mole % AA and 15 mole % of DADMAC.
X1	A copolymer being 35.0 % active in solution form and formed of 69 mole % of AA, and 31 mole % of DADMAC.
Y1	A terpolymer being 20.0 % active in solution form and formed of 15% by weight of MAPTAC, 46 % by weight AA and 8 % by weight of DADMAC.
Z1	A terpolymer being 10.0 % active in solution form and formed of 30 mole % of AA, and 20 mole % of MAPTAC and 50 mole % AM.
A2	A terpolymer being 10.0 % active in solution form and formed of 30 mole % of AA, and 20 mole % of MAPTAC and 50 mole % VP.
B2	A copolymer being 35.0 % active in solution form and formed of 40 wt % AA, and 60 wt % of DADMAC.
C2	A copolymer being 35.0 % active in solution form and formed of 10 wt % AA, and 90 wt % of DADMAC.
D2	A copolymer being 45.0 % active in solution form and formed of 15 wt % AA, and 85 wt % of DADMAC.
E2	A terpolymer being 20.0 % active in solution form and formed of 35 mole % of AA, and 34 mole % of VP and 31 mole % DADMAC.
E3	An anionic flocculant copolymer being 28.5% active in emulsion form and formed of 70% AM and 30% AA.

Products A, B, C, D, E, F, G, I, J, K, N, and N1 are available from Calgon Corporation, Pittsburgh, PA. and/or ECC International Inc., Atlanta, GA. Product O1 is available from Nalco Chemical Company. Products D1 and 5 K1 are available from ECC International Inc. Product H is available from BASF Corporation Dispersions and Paper Chemicals.

Products A, B, and C are preferred terpolymer polyampholyte coagulants of the invention with Product L being the preferred flocculant. Other terpolymers, such 10 as H1, P1, Q1, R1, S1, T1, U1, V1, W1, Y1, Z1, A2 and E2 are additional terpolymer polyampholytes of the invention, while the chemistries for B2, C2 and D2 are preferred copolymer polampholytes of the invention.

15 Note: All dosages herein relating to the invention and in the following examples are expressed as active based on lb./ton of dry pulp.

Polyampholyte - Retention/Drainage/Formation

20 Some of the polymers including the polyampholytes of the invention listed herein above were used as a retention/drainage/formation aid in the papermaking process:

Example 1

25 A laboratory vacuum drainage test was conducted on newsprint stock to compare the polyampholyte coagulants of the invention with other coagulant products, some of which are available from ECC International Inc. The furnish was obtained from a paper mill and comprised 75 to 80% fine TMP (thermomechanical pulp), 5% kraft, 5% PCW (Post Consumer Waste), and 10 to 15% broke. The paper 30 machine was running at 4100 to 4300 feet per minute, and the conditions were as follows:

35.1%	First Pass Retention (FPR)
13.9%	Fines Retention
1.24%	Headbox Consistency
0.81%	Tray Consistency
5	-785 μ eq/l HB Total Mutek Charge
	-253 μ eq/l HB Filtered Mutek Charge
	2900 Conductivity

Thin stock was taken from the paper machine before
10 any polymers were added. An aliquot of stock was mixed
in a Britt Jar with a sheet of plastic over the wire
while the flocculants and coagulants were added. The
mixing sequence was as follows:

	<u>Time</u>
15	0 Sec. 1200 RPM
	10 Sec. Add Flocculant (pre-shearing stage)
	18 Sec. 800 RPM (representing a shearing stage)
	20 Sec. Add Coagulant (post shearing stage)
	30 Sec. Stop Mixer

20 The vacuum drainage test (VDT) was conducted using
the Buchner Funnel, a vacuum pump, 24.5" Hg, and a 500 ml
glass vacuum flask. The Vac. 400, which represents time
(seconds) in which 400 ml of stock is drained from the
25 flask, was recorded. The flocculant (Products L and M)
was used at 0.25 (active) lb./t., and the coagulants were
used at 1.0 (active) lbs./ton.

30 The results are shown in Table 1 where the drainage
rate for the stock containing Products B and C (Items 12
and 13) of the invention was less than that for the stock
samples containing other types of coagulants. These
stock samples containing Products B and C also showed a
much higher improvement percentage when compared to the

other types of coagulants and when using "flocculant only" as the reference basis.

TABLE 1

#	(Product) Floc.	Active. lbs./ ton	(Product) Coag.	Active lbs./ ton	Time (Sec.) Vac 400	With Product L
						% Improvement Over Blank
1	Blank	0	Blank	0	73	-26.7
2	L	0.25	--	0	58	0.0
3	L	0.25	K	1	61	-4.4
4	L	0.25	J	1	61	-3.7
5	L	0.25	G	1	54	8.8
6	L	0.25	F	1	45	24.6
7	L	0.25	D	1	41	31.7
8	Blank	0	Blank	0	75	-24.0
9	L	0.25	--	0	61	-0.2
10	L	0.25	E	1	43	29.8
11	L	0.25	I	1	60	2.8
12	L	0.25	C	1	40	35.6
13	L	0.25	S	1	46	26.4
14	L	0.25	H	1	60	5.3
15	M	0.25	H	1	60	5.9
16	M	0.25	--	0	73	-13.7
17	Blank	0	Blank	0	80	-23.9
18	M	0.25	--	0	65	0.0

5 A second test was done similar to that above where the coagulants were used at 0.5, 1.0, 1.5 and 2.0 (active) lbs./ton. Table 2 shows these results were the samples for Items 8-12 with Products C and L, the coagulant/flocculant system of the invention show the best drainage rates at 37 sec., 32 sec., 30 sec., and 29 sec., respectively when compared to the samples containing other types of coagulants.

10

TABLE 2

#	(Product) Floc.	Active lbs. /ton	(Product) Coag.	Active lbs. /ton	Time (Sec.) Vac 400	% Improvement Over Blank
1	Blank	0	-	0	69	0
2	L	0.25	--	0	54	21.9
3	L	0.5	--	0	43	37.9
4	L	0.25	D	0.5	39	43.8
5	L	0.25	D	1	34	51.1
6	L	0.25	D	1.5	33	52.6
7	L	0.25	D	2	32	54.2
8	L	0.25	C	0.5	37	47.1
9	L	0.25	C	1	32	54.3
10	L	0.25	C	1.5	30	57.3
11	L	0.25	C	2	20	58.8
12	L	0	--	0	71	-0.7
13	L	0.25	--	0	53	25.0
14	L	0.5	--	0	47	33.6
15	L	0.25	E	0.5	44	37.9
16	L	0.25	E	1	39	45.1
17	L	0.25	E	1.5	35	50.8
18	L	0.25	E	2	34	52.3
19	L	0.25	F	0.5	46	35.6
20	L	0.25	F	1	40	44.1
21	L	0.25	F	1.5	37	48.4
22	L	0.25	F	2	37	48.5
23	L	0	--	0	72	0.0
24	L	0.25	--	0	55	23.8
25	L	0.25	H	0.5	56	22.5
26	L	0.25	H	1	49	32.3
27	L	0.25	H	1.5	45	38.0
28	L	0.25	H	2	44	39.5

Example 2

5 Laboratory testing for retention and drainage was conducted on recycled newsprint furnish containing about 75% deinked pulp (DIP) and about 25% thermomechanical pulp (TMP).

10 For the vacuum drainage test, several 500 ml aliquot samples of stock from the headbox were mixed in a Britt Jar sealed with cellophane over the screen while the coagulants and flocculants were added. The mixing sequence was the same as that for Example 1, i.e., the flocculant added pre-screen and the coagulant added to simulate post-screen (low shear) mixing, except for the 15 high shearing stage being 1500 rpm instead of 800 rpm.

5 The stock samples containing flocculant and coagulant were poured into a Buchner Funnel with Whatman 41 Filter Paper in place. The vacuum connected to a 500 ml vacuum flask was turned on. The volume (ml) of water draining in 30 seconds through the filter paper was recorded and used as a measurement of performance.

10 The results are shown in Table 3 where Product B of the invention and Product E give comparable results relative to each other and the best drainage and percent improvement results when compared to other types of coagulant/flocculant systems.

15

TABLE 3
Vacuum Drainage

Test Coag.	Test Floc.	Feed Rate (lbs./ton)		Shear Rate (rpm)	Drainage mls/30 sec.	Percent Improvement Over No Aid
--	No Aid	--	--	1500	173	--
--	T	--	1	1500	193	11.6
E	T	2	1	1500	242	39.9
K	T	2	1	1500	212	22.5
X	T	2	1	1500	231	33.5
B	T	2	1	1500	242	39.9
E	T	2	2	1500	246	42.2
K	T	2	2	1500	226	30.6
X	T	2	2	1500	238	37.6
B	T	2	2	1500	246	42.2

20

First pass retention (FPR) was tested using TAPPI Test Method T269. Stock was collected from the discharge of the primary fan pump. 500 ml samples were poured into a Britt Jar with a 70 mesh screen while stirring the stock at 1500 rpm. The mixing time/speed sequence was similar to that used for the drainage test herein in order to simulate chemical addition points in a paper machine.

25

The results are shown in Table 4.

TABLE 4
Retention

Test Coag.	Test Floc.	Feed Rate (lbs./ton)		Shear Rate (rpm)	First Pass Retention		
		Coag. (Product)	Floc. (Product)		Fines	Ash	Total
--	No Aid	--	--	1500	21.5	18.8	57.9
--	S	--	0.5	1500	28.2	31.5	61.6
--	T	--	0.5	1500	30.6	34.4	62.8
--	No Aid	--	--	1500	24.0	20.7	59.3
--	S	--	1	1500	27.3	30.5	61.0
--	T	--	1	1500	33.4	38.7	64.3
E	S	2	1	1500	31.3	33.7	63.2
E	T	2	1	1500	35.7	39.8	65.5
V	S	2	1	1500	27.7	30.7	61.3
V	T	2	1	1500	32.8	38.3	64.0
C	S	2	1	1500	28.8	32.0	61.9
C	T	2	1	1500	33.1	38.5	64.1
A	S	2	1	1500	27.5	30.9	61.2
A	T	2	1	1500	32.4	37.7	63.8
W	S	2	1	1500	26.4	30.0	60.6
W	T	2	1	1500	31.1	35.9	63.1
D	S	2	1	1500	28.3	30.7	61.6
D	T	2	1	1500	31.5	36.0	63.3
J	S	2	1	1500	28.2	31.0	61.5
J	T	2	1	1500	34.1	38.4	64.7
G	S	2	1	1500	28.5	31.7	61.7
G	T	2	1	1500	34.2	39.4	64.7
K	S	2	1	1500	28.6	32.4	61.8
K	T	2	1	1500	35.7	40.8	65.6
X	S	2	1	1500	29.9	32.8	62.5
X	T	2	1	1500	35.0	39.5	65.2
Y	S	2	1	1500	29.0	32.1	62.0
Y	T	2	1	1500	32.5	38.0	63.8
F	S	2	1	1500	30.2	31.7	62.6
F	T	2	1	1500	30.7	34.4	62.9
E	S	2	1	1500	32.4	36.3	63.8
B	T	2	1	1500	38.5	44.6	67.1

Products A, B, and C (coagulants) of the invention, when combined with Product T (flocculant), show high ash retention at 37.7%, 44.6% and 38.5% FPR with the highest for all dual polymer system being for Products B and T at 44.6% FPR. These retention and drainage results indicate that in the invention, filler retention should be realized along with increased drainage.

Example 3

A retention aid study was performed for a high conductivity linerboard furnish. The furnish consisted of 100% unbleached hardwood kraft pulp.

5 Britt jar testing was used to screen furnish for the best flocculant/coagulant system starting with an initial conductivity of 2800 μ mhos, and increasing to 3800 and 4500 μ mhos by adding sodium sulfate solution.

Procedure

10 Headbox stock with a consistency of 1.0% was heated to 120°F, and the pH was adjusted to 5.0 with alum. The initial conductivity measured 2800 μ mhos. Each 500 ml aliquot of stock was poured into a vaned Britt jar with 70 mesh screen. First the stock was mixed with 10% clay 15 filler followed by the coagulant. After mixing the stock with the clay filler and coagulant for 15 seconds at 600 rpm, the mixer speed was increased to 1200 rpm for 10 seconds. The flocculant was added to the stock and the mixer speed was reduced to 600 rpm and mixed for an 20 additional 10 seconds. After 35 seconds total mixing, the pinch clamp was removed and 100 ml of filtrate was collected in a graduate cylinder. The filtrate was flocked with a coagulant (Product B) to help retain the fines and the clay filler and to aid in the speed 25 filtration. After filtering and drying, the filter pads were ashed at 900°C for 30 minutes. The dry and ash weights of the filtrate solids were recorded and used to calculate fines, ash, and total first pass retention.

30 The results are shown in Table 5. Based on this study, at a high conductivity of 4500 μ mhos, Product Z gave the best total first pass retention percentage, i.e. 79.1 for Product B (Item 28) and 79.0 for Product H1 (Item 29), which are the coagulants of the invention. Products B and H1 combined with Product Z as the

flocculant also gave the best fines retention (Items 28 and 29).

TABLE 5
Britt Jar Test Results

		Coagulant			Flocculant						% First Pass Retention			
Test No.	D1	Prod	lbs./ton	Act.	RPM	Prod	lbs./ton	Act.	RPM	Coll. Fines (T) (g/100 ml)	Coll. Ash (V) (g/100 ml)	Fines	Ash	Tot.
2800 μ hos Conductivity														
+	10%	No Aid	--	1200	--	--	600	0.2970	0.0606	29.3	13.7	70.1		
+	10%	--	--	1200	I1	0.5	600	0.2645	0.0513	37.0	26.9	73.4		
+	10%	--	--	1200	J1	0.5	600	0.2541	0.0452	39.5	35.6	74.4		
+	10%	--	--	1200	L	0.5	600	0.2423	0.0482	42.3	31.3	75.6		
+	10%	--	--	1200	Z	0.5	600	0.2226	0.0342	47.0	51.3	77.6		
+	10%	--	--	1200	A1	0.5	600	0.2284	0.0403	45.6	42.6	77.0		
+	10%	--	--	1200	D1	0.5	600	0.2468	0.0466	41.3	33.6	75.2		
3800 μ hos Conductivity														
+	10%	--	--	1200	--	--	600	0.2952	0.0592	29.7	15.7	70.3		
+	10%	--	--	1200	I1	0.5	600	0.2515	0.0432	40.1	38.5	74.7		
+	10%	--	--	1200	J1	0.5	600	0.2358	0.04	43.9	43.0	76.3		
+	10%	--	--	1200	L	0.5	600	0.2371	0.044	43.6	37.3	76.2		
+	10%	--	--	1200	Z	0.5	600	0.2234	0.0349	46.8	50.3	77.5		
+	10%	--	--	1200	A1	0.5	600	0.2232	0.0383	46.9	45.4	77.6		
+	10%	--	--	1200	D1	0.5	600	0.2445	0.0465	41.8	33.8	75.4		
4500 μ hos Conductivity														
+	10%	--	--	1200	No Aid	--	600	0.2958	0.063	29.6	10.3	70.3		
+	10%	--	--	1200	B1	0.5	600	0.2133	0.0275	49.2	60.8	78.6		
+	10%	--	--	1200	Z	0.5	600	0.2306	0.0349	45.1	50.3	76.8		
+	10%	--	--	1200	A1	0.5	600	0.2243	0.0385	46.6	45.2	77.4		
+	10%	J	0.5	1200	Z	0.5	600	0.2268	0.0335	46.0	52.3	77.2		
+	10%	K	0.5	1200	Z	0.5	600	0.2238	0.0334	46.7	52.4	77.5		
+	10%	C	0.5	1200	Z	0.5	600	0.2156	0.0314	48.7	55.3	78.3		
+	10%	Y	0.5	1200	Z	0.5	600	0.2116	0.0299	49.6	57.4	78.7		
+	10%	D	0.5	1200	Z	0.5	600	0.2162	0.0316	48.5	55.0	78.3		
+	10%	G	0.5	1200	Z	0.5	600	0.2124	0.0294	49.1	58.1	78.5		
+	10%	E1	0.5	1200	Z	0.5	600	0.2226	0.0371	46.2	47.2	77.3		
+	10%	A	0.5	1200	Z	0.5	600	0.2214	0.0344	47.3	51.0	77.7		
+	10%	G1	0.5	1200	Z	0.5	600	0.2149	0.0321	48.8	54.3	78.4		
+	10%	E	0.5	1200	Z	0.5	600	0.208	0.0303	50.5	56.8	79.1		
+	10%	H1	0.5	1200	Z	0.5	600	0.2088	0.034	50.3	56.7	79.0		

5

10

As described in Principles of Wet End Chemistry by William E. Scott, PhD., TAPPI Press, Atlanta, GA, 1996, p. 105, low molecular weight (100,000-1,000,000) cationic coagulants with high charge density (> 4 meq charge/gram) are mixed with anionic particles (aqueous cellulosic furnish) to form a positive patch charge on the surface of the anionic particles. After the cationic coagulant is adsorbed onto the surface of the anionic particles, collision of the positive patch with a

negatively charged surface on another particle leads to agglomeration.

The inventors have found that in certain paper furnishes the polyampholyte coagulant polymer (lower overall cationic charge) of the invention performs significantly better than the high charge density coagulants of the prior art. The above Examples 1-3 exemplify this.

10 Polyampholyte As An Attachment Aid In
Coated Broke And A Retention/Drainage Aid

Example 4

15 A second aspect of the invention pertains to the use of a polyampholyte coagulant of the invention for treating coated broke and then using the treated coated broke as a portion of the furnish in making paper and adding the polyampholyte coagulant of the invention as a retention and/or drainage aid in the papermaking process.

20 Coated broke is used in many fine or other paper furnishes. The coating applied to the base sheet may contain this coated broke comprising pigments and binders, both of which can cause problems in the sheet forming process. As explained hereinabove, the binders can agglomerate to form sheet defects or deposits on the 25 machine. The coating pigments in the coated broke are more difficult to retain than wet end pigments in view of their small size. The polyampholyte coagulant of the invention as disclosed hereinabove for treating coated broke has been found to be an effective way for 30 significantly reducing white pitch deposits and poor coating pigment retention problems whereby the pigments and the binders are attached to the fiber in the pulp.

35 The polyampholyte of the invention was used as an attachment aid for the white pitch or stickies and the mineral pigments from coated broke where the white pitch

or stickies and the pigments are attached to the longer fibers instead of depositing on sites in the paper machine.

Several samples of coated broke obtained from a 5 coated broke tank of a paper machine of a commercial paper mill, and laboratory vacuum drainage and turbidity (determines retention) tests were conducted. A turbidity test was done to show the performance of a coagulant and its ability to attach colloidal and fine particles in the 10 coated broke onto the fiber in making the paper. For this test, 100 grams of coated broke in slurry form was placed into small beakers and treated with the polyampholyte coagulant of the invention and several 15 other types of coagulants. Each sample was mixed for 1 minute and then filtered through a No. 4 Whatman Filter Paper using a standard (inverted cone) funnel. The turbidity of the filtrate was then measured using a Hach TR 2000 Turbidimeter that measures turbidity in National 20 Turbidity Units (NTU). The cationic demand was measured using a Mutek Particle Charge Detector.

The dosages for the coagulant was either 2.75 (active) pounds per ton (dry weight of solids in furnish), or 3.75 (active) pounds per ton (dry weight of solids in the furnish).

25 The results of the turbidity (retention) tests are shown in Table 6. The "lowest" turbidity level is produced by the product and the dosage which attached the most colloidal and fine material onto the fiber.

TABLE 6

#	Product	Active lbs./ton	Turbidity (NTU)	Cationic Demand (meq./L)
1	Blank	--	1320	-710
2	O	3.7	56	-548
3	J	3.7	52	-272
4	K	3.7	121	-300
5	G	3.7	173	-510
6	F	3.7	113	-480
7	D	3.7	53	-580
8	E	3.7	182	-560
9	I	3.7	450	-660
10	C	3.7	36	-580
11	B	3.7	216	-590
12	H	3.7	97	-510
13	Blank	--	1470	-740
14	O	2.75	221	--
15	J	2.75	253	--
16	K	2.75	279	--
17	G	2.75	470	--
18	F	2.75	320	--
19	D	2.75	155	--
20	E	2.75	480	--
21	I	2.75	560	--
22	C	2.75	68	--
23	B	2.75	505	--
24	H	2.75	120	--
25	Blank	0	1580	--

Table 6 shows that the lowest filtered turbidity was 5 Product C (36 NTU) at a dosage of 3.7 (active) 10 solution, which Product C is one of the preferred 15 polyampholytes of the present invention. This Product C is a solution terpolymer with an 8% active AM/AA/DMDAAC 20 at 15:5:50 weight % polymer composition. The cationic 25 demand for the furnish containing Products B and C (Items 30 11 and 10) of the invention in Table 6 is -590 and -580 35 meq./L), respectively which reduced the furnish charge 40 to less than some of the standard coagulants presently 45 used in the paper mills.

The polyampholyte coagulant of the invention was then used as a retention/drainage aid in the papermaking process.

For the vacuum drainage tests, stock from the mix 5 chest (tank) was diluted to headbox consistency (~1.0%). The headbox stock contains a portion of the coated broke used for the turbidity test.

The test procedure was similar to that used in Example 1, except that the coagulant was added during 10 high shear mixing (simulated screening or shearing stage) and the flocculant was added during low shear mixing. The dosage of the coagulant was 1.0 (active) lb./ton based on the dry solids in the aqueous cellulosic furnish and the dosage of the flocculant was 0.25 (active) 15 lb./ton based on the dry solids in the aqueous cellulosic furnish.

The results are shown in Table 7 for the different coagulant products tested with the same flocculant (Product L). Products B and C of the invention worked as 20 well as if not better than some of the standard coagulants with a drainage rate of 24 and 27.4, respectively, i.e., the lower numbers representing a faster drainage time.

TABLE 7

#	Pre-Screen	Active lbs./ ton	Post Screen	Active lbs./ ton	Time (Sec.) Vac 400	% Improvement Over Blank
1	Blank	--	--	0	28	0
2	--	--	L	0.25	23	19.9
3	N	1	L	0.25	27	8.3
4	J	1	L	0.25	25.3	16.1
5	O	1	L	0.25	23.5	23.8
6	K	1	L	0.25	28.4	10.0
7	F	1	L	0.25	24.6	23.8
8	G	1	L	0.25	20.2	38.8
9	D	1	L	0.25	21.7	35.6
10	E	1	L	0.25	22.6	34.4
11	I	1	L	0.25	23.8	32.3
12	C	1	L	0.25	27.4	23.6
13	B	1	L	0.25	24	34.4
14	H	1	L	0.25	27.9	25.2
15	--	--	--	0	38	0.0
16	--	--	--	0.25	27.6	28.7

From the above results, it can be seen that there is a possibility that coated broke treated with the polyampholyte of the invention prior to its being added to the paper furnish can decrease the turbidity and increase the drainage rate of the fiber mat on the wire in the paper forming process.

10

Polyampholyte Added To White Water

A third aspect of the invention pertains to the use of a polyampholyte coagulant of the invention in a saveall application. It has been found by the inventors that polyampholyte coagulants of the invention are very effective in clarifying white water for reuse either in the paper machine or in the pulp mill. The white water is treated with the polyampholyte coagulant of the invention to aid in settling the solids or if air flotation is used in floating the solids for removal from the saveall.

15

20

The polyampholyte coagulant of Example 5 was added to the saveall influent to settle the fibers and fines out of the recycled white water.

Example 5

Samples of 100 ml of saveall influent (process water from the paper machine) from a commercial paper mill were placed in clear, clean jars. All the polymers were 5 diluted to 1.0% solutions. Products L and L1 were taken from the age tank at the paper mill and were believed to contain about 1% solids. 1.0 ml of dilute polymer was added to each jar. Each jar was shaken for several seconds and allowed to settle. The clarity of the water 10 in each jar was visually observed and given a "poor to excellent" rating.

The results are shown in Table 8.

TABLE 815 Jar Test Results For Saveall Influent

Polymer Product	Dose (ppm)	Water Clarity (2 min. settling time)
B	100	Good
B	100	Excellent
B	100	Excellent
L1	100	Fair
L	100	Fair
J	100	Poor
M1	100	Poor

The samples with the highest clarity showed the best polymer performance. In Table 8, the best clarity occurred with the use of Product B which is one of the 20 preferred polyampholyte (terpolymer) coagulants of the invention.

Example 6
Pilot Pressing StudyFurnish Description for Fine Paper

25 13% Softwood Bleached Kraft
44% Hardwood Bleached Kraft
36% Coated Broke
7% Post Consumer Waste (Mixed Office Waste)

Furnish Preparation:

5 Thick stock and white water from an alkaline fine paper mill was used for this lab study. Furnish of the above proportions was combined with mill white water to dilute the thick stock to 1.0 % consistency (pH = 7.5).
10 A 630 ml aliquot was used for the Control and 540 ml aliquot for the handsheets containing retention aid. The target sheet weight was 5.4g (= 100 lb/3000ft² coated or about 80lb raw stock weight) per 8"x8" sheet. The starch was a cationic starch obtained under the trade name HiCat 142 from the National Starch Company. About 2ml of starch of a 1.9% solution (= 14 lbs/ton) was used in this example.

15 The 1.0 % consistency stock was mixed with flocculant and coagulant using a Britt Jar type (variable speed mixer) according to the procedure below.

20 Handsheet Procedure: (Williams Sheet Mold) for Pilot Pressing Study

		<u>Elapsed Time</u>
25	1. Measure out stock.	
	2. Set agitator speed to 700 rpm.	
	3. Add starch to stock and mix. (Start timer)	0 sec.
	4. Increase speed to 1200 rpm.	40 sec.
	5. Add first polymer.	1 min.
	6. Reduce speed to 700 rpm.	1 min. 10 sec.
30	7. Add second polymer and mix.	1 min. 10 sec.
	8. Shut off mixer	1 min. 15 sec.
	9. Pour stock into handsheet mold already filled with water.	

10. Mix stock with hand agitator. Drain sheet mold.
Place two blotters on top of sheet and press with 5
lb. Williams "rolling pin".
11. Place sheets from each set in air-tight plastic bag.
- 5 12. Handsheets were then individually weighted and run
through pilot sheet press.

Pressing Conditions

10 Press Speed: 1750 fpm

10 Press Load (pounds/linear inch- PLI)

10 1st Press: 425

10 2nd Press: 450

10 3rd Press: 550

15 Handsheets were run in sets of five. The weight of
each sheet was measured before the first press and after
pressing through each nip. Oven dry weight was determined
to calculate press solids. Brightness was measured on a
Technidyne Color One Touch brightness meter according to
Tappi Test Method T-452.

20 The results of the press solids (%) and brightness
levels for the a terpolymer polyampholyte of the
invention (Product B) and other types of coagulants are
shown in Figure 1. Figure 1 shows that for fine paper,
25 which contains very little recycled paper, the % press
solids in the 3rd press for the polyampholyte of the
invention (Product B) are acceptable, i.e. about 39.5%,
and the brightness levels are greater than some of the
other types of coagulants, i.e. equal to or greater than
30 85.5. It is also to be noted that in conventional
practice, the coagulant is added first followed by the
focculant. In the samples for Figure 1, in all but the
last case, the focculant was added first followed by the
coagulant. In the last case, ie Conv.F, the coagulant

(Product F) was added first followed by the focculant. All samples, except the Blank sample, of Figure 1 contain 0.28 lbs/ton active anionic flocculant of Product E3.

5

Hypotheses:

Polyampholyte Coagulants and Brightness:

10

Amphoteric coagulants provide a brightness increase in furnishes containing either recycle fiber and or coated broke and virgin filler possibly by two different mechanisms. The first mechanism is for furnishes containing recycled fiber and the second mechanism concerns the degree of agglomeration and distribution of filler within the sheet.

15

1. Recycled Fiber Effect On Brightness:

20

Even though recycled fiber is "deinked", it still contains some black ink and colored ink particles. When standard coagulants, i.e polyamine, DADMAC or polyethyleneimine (PEI), plus a flocculant are added to the furnish, the brightness of the resulting paper decreases as the dosage of the coagulant is increased. As the dosage of the coagulant is increased, more of the ink from the white water is retained. The high charge density of these coagulants entraps (retains more of the ink that would be retained with lower charged polymers. The brightness of the sheet drops with greater ink retention. Polyampholyte coagulants of the invention on the other hand, using a combination of molecular weight and lower overall cationic charge, retain the recycled and virgin filler without retaining the ink so the brightness of the sheet remains higher.

25

30

2. Filler Distribution/Agglomeration as a Function of Polyampholyte Chemistry

The second part of the theory regarding higher sheet brightness deals with the agglomeration and distribution of the filler in the sheet. Filler agglomeration is significantly less in handsheets containing a polyampholyte coagulant compared to sheets containing an equal dosage of a cationic coagulant. SEM photomicrographs (not included herein) showing the distribution of filler in the x-y plane show much larger agglomerates of filler for sheets containing DADMAC, polyamine or PEI coagulants than for a polyampholyte coagulant. The polyampholyte of course must be of sufficient molecular weight to retain the filler or poor filler retention will result.

The preferred polyampholyte chemistry consists of a terpolymer containing acrylamide to help build molecular weight providing good filler retention. Figure 4 shows the data for a number of copolymer polyampholytes that do not show a drop in brightness as the dosage of the coagulant was increased, however, the sheet brightness is also low denoting poor filler retention.

Super Calendered (SC) /Newsprint Grades

25 Furnish

30% Deinked Pulp

30% Refiner Mechanical Pulp

40% Chemimechanical Pulp

30 1. Make handsheets using Britt Jar mixer to mix stock and polymer. Use 0.3, 0.6, and 0.9 #/t active for the coagulants and 0.3 #/ton active for the polymer Product S. Use new 80 mesh screens for the handsheets.

2. Test handsheets for sheet weight, formation, brightness, predicted opacity (sheet scattering coefficient and so forth).
3. Brightness will be the most important criteria for measuring the performance of the polyampholyte polymers. Brightness was measured on a Technidyne Color One Touch brightness meter according to Tappi Test Method T-452.

10 Handsheet Procedure:

1. Dilute the alkaline furnish to 0.5% consistency with tap water. Measure and record pH (target 7.5-7.8).
2. Pour out ~400 ml of stock into the 500ml square jars.
3. Turn on agitator at 1200rpm.
4. Add coagulant and mix for 15 seconds.
5. Reduce speed to 800 rpm then add 0.3 #/t active 954.
6. Mix stock/polymers 15 more seconds, then shut off agitator.
7. Pour stock into handsheet mold, fill to top mark with water and mix with hand agitator.
8. Drain sheet mold. Press handsheet with new press felt. Dry handsheets with screen toward dryer drum (210 deg. F; 4 min./revolution).

25 The results are depicted in Figures 2-4. These results show that all terpolymer polyampholytes of the invention containing acrylamide had the highest brightness levels. Products N and K show that as the dosage of the coagulant increased, there was a significant decrease in brightness; whereas, the polyampholytes of the invention show either a slight decrease in brightness or no decrease in brightness as the coagulant dosage was increased.

30 35 The brightness decrease of the handsheets containing Products N and K was possibly the result of two factors. First, as the dose of Products N and K was increased, the amount of ink retained from the recycle fiber was also increased. Secondly, increasing the dose of Products N

40

and K excessively agglomerated the filler in the handsheets to the extent that the optical efficiency of the filler (light scattering) was reduced and thus the brightness level was decreased.

5 The polyampholytes of the invention fall into two groups in terms of performance, i.e handsheet brightness and filler retention. The terpolymers shown in Figures 2 and 3 had higher brightness (above 57.0) than the copolymers shown in Figure 4. The main difference in 10 polymer chemistry between the copolymers and the terpolymers is the presence of acrylamide in the terpolymers which tends to boost the molecular weight of the polymer. As long as the polymer has the 15 polyampholyte functionality and acrylamide for increased molecular weight, then the brightness of the paper containing the polyampholyte of the invention will not drop with increasing polymer dosage. Also, the filler retention with the acrylamide containing polyampholytes 20 will remain high.

25 The brightness of handsheets containing the polymer polyampholytes show the same trend of retaining brightness as the polyampholyte copolymer is increased but the copolymers do not retain the filler nearly as well.

30 Whereas particular embodiments of the present invention have been described for purposes of illustration, it will be evident to those skilled in the art that numerous variations and details of the invention may be made without departing from the invention as defined by the appended claims.

WHAT IS CLAIMED IS

1. A paper or paperboard furnish containing a retention and drainage aid composition, comprising:
 - a polyampholyte coagulant.
- 5 2. The furnish of Claim 1 wherein said polyampholyte coagulant comprises at least two monomers.
3. The furnish of Claim 1 wherein said polyampholyte coagulant is a copolymer comprising an anionic monomer and a cationic monomer.
- 10 4. The furnish of Claim 1 wherein said polyampholyte coagulant has a weight average molecular weight ranging from about 10 thousand to about 20 million.
5. The furnish of Claim 1 wherein said polyampholyte coagulant comprises at least one anionic monomer selected from the group consisting of acrylic acid, homologues of acrylic acid, sodium acrylate, vinyl sulfonic acid, sodium vinyl sulfonate, itaconic acid, sodium itaconate, 2-acrylamido-2-methylpropane sulfonic acid, sodium salt, acrylamidoglycolic acid, 2-acrylamido-20 2-methylbutanic acid, 2-acrylamido-2-methylpropanephosphonic acid, sodium vinyl phosphonate, allyl phosphonic acid, and mixtures thereof.
- 20 6. The furnish of Claim 5 wherein said polyampholyte coagulant further comprises at least one cationic monomer selected from a group consisting of quaternary dialky diallyl ammonium chloride, methacryloyethyl trimethyl ammonium chloride, quaternized derivatives of dimethyl amino ethyl acrylate, dimethyl amino ethylacrylate, dibutyl aminoethyl methacrylate, dimethyl amino methyl acrylate, dimethyl amino methyl methacrylate, diethyl amino propyl methacrylate, acryloyloxyethyl trimethyl ammonium methosulfate, amino methylated polyacrylamide, and combinations thereof.

7. The furnish of Claim 6 wherein said anionic and cationic monomers comprise a terpolymer which further comprises at least one nonionic monomer selected from the group of N-vinylamide, N-alkylacrylamide, vinyl acetate, 5 vinyl alcohol, acrylate esters, diacetone acrylamide, N,N-dialkyl- acrylamide.

8. The furnish of Claim 1 wherein said polyampholyte coagulant is a terpolymer consisting of (a) a nonionic monomer, (b) an anionic monomer, and (c) a cationic monomer in a weight percent ratio for a:b:c ranging from 10 about 1:1:98 to about 1:98:1 to about 98:1:1 based on the dry weight of said polyampholyte coagulant.

9. The furnish of Claim 1 wherein said polyampholyte coagulant is present in the paper furnish in an amount of 15 at least 0.0025% by weight based on the dry weight of the solids in the furnish.

10. The furnish of Claim 1 wherein said polyampholyte coagulant comprises a copolymer consisting of (a) an anionic monomer and (b) a cationic monomer in a weight percent ratio for a:b ranging from about 1:99 to 99:1 20 based on the dry weight of said polyampholyte coagulant

11. The furnish of Claim 1 wherein said retention and drainage aid composition further comprises a water soluble flocculant.

25 12. The furnish of Claim 1 wherein said polyampholyte coagulant consists of acrylamide (AM), acrylic acid (AA), and dimethyl diallyl ammonium chloride (DADMAC) in a weight percent ratio ranging from about 48:2:50 to about 25:25:50 based on the dry weight of said polyampholyte coagulant.

30 13. The furnish of Claim 1 wherein said polyampholyte coagulant consists of acrylamide (AM), 2-acrylamido-2-methylpropane sulfonic acid (AMPS), and dimethyl diallyl

ammonium chloride (DADMAC) in a weight percent ratio of about 41:13:46.

14. A method for producing paper products, the steps comprising:

5 prior to a first shearing stage or after the last shearing stage, adding a polyampholyte coagulant to the paper furnish in an amount of at least 0.0025% by weight based on the dry weight of the solids in the furnish to improve the retention/drainage properties of a
10 paper web in producing said paper product.

15. The method of Claim 14, the steps further comprising:

before adding the polyampholyte coagulant to the paper furnish, adding a water soluble flocculant to the paper furnish.

16. A paper product made with the polyampholyte coagulant of Claim 1 and having at least improved optical properties, and improved formation, drainage and retention.

17. A method for treating coated broke comprising white pitch, fillers, and fibers, the steps comprising:

adding a polyampholyte coagulant to the coated broke to attach at least the white pitch and fillers to the fibers.

18. The method of Claim 17 wherein said polyampholyte coagulant comprises at least two monomers

19. The method of Claim 17 wherein said polyampholyte coagulant is a copolymer comprising an anionic monomer and a cationic monomer.

20. The method of Claim 17 wherein said polyampholyte coagulant has a weight average molecular weight ranging from about 10 thousand to about 20 million.

21. The method of Claim 17 wherein said polyampholyte coagulant consists of acrylamide (AM), acrylic acid (AA), and dimethyl diallyl ammonium chloride (DADMAC) in a weight percent ratio ranging from about 48:2:50 to about 5 25:25:50 based on the dry weight of said polyampholyte coagulant.

22. The furnish of Claim 17 wherein said polyampholyte coagulant consists of acrylamide (AM), 2-acrylamido-2-methylpropane sulfonic acid (AMPS), and dimethyl diallyl 10 ammonium chloride (DADMAC) in a weight percent ratio of about 41:13:46.

23. The method of Claim 17 wherein said polyampholyte coagulant is present in the paper furnish in an amount of at least 0.0025% by weight based on the dry weight of the 15 solids in the furnish.

24. The method of Claim 17 wherein said polyampholyte coagulant comprises at least one anionic monomer selected from the group consisting of acrylic acid, homologues of acrylic acid, sodium acrylate, vinyl sulfonic acid, 20 sodium vinyl sulfonate, itaconic acid, sodium itaconate, 2-acrylamido-2-methylpropane sulfonic acid, sodium salt, acrylamidoglycolic acid, 2-acrylamido-2-methylbutanic acid, 2-acrylamido-2-methylpropanephosphonic acid, sodium vinyl phosphonate, allyl phosphonic acid, and mixtures 25 thereof.

25. The method of Claim 24 wherein said polyampholyte coagulant polymer further comprises at least one cationic monomer selected from a group consisting of quaternary dialky diallyl ammonium chloride, methacryloyethyl 30 trimethyl ammonium chloride, quaternized derivatives of dimethyl amino ethyl acrylate, dimethyl amino ethylacrylate, dibutyl aminoethyl methacrylate, dimethyl amino methyl acrylate, demethyl amino methyl methacrylate, diethyl amino propyl methacrylate,

acryloyloxyethyl trimethyl ammonium methosulfate, amino methylated polyacrylamide, and combinations thereof.

26. The method of Claim 25 wherein said anionic and cationic monomers comprise a terpolymer which further 5 comprises at least one nonionic monomer selected from the group of N-vinylamide, N-alkylacrylamide, vinyl acetate, vinyl alcohol, acrylate esters, diacetone acrylamide, N,N-dialkyl- acrylamide.

27. The method of Claim 17 wherein said polyampholyte 10 coagulant is a terpolymer consisting of (a) a nonionic monomer, (b) an anionic monomer, and (c) a cationic monomer in a weight percent ratio for a:b:c ranging from about 1:1:98 to about 1:98:1 to about 98:1:1 based on the dry weight of said polyampholyte coagulant polymer.

28. The method of Claim 17 wherein said polyampholyte coagulant polymer comprises a copolymer consisting of 15 (a) an anionic monomer and (b) a cationic monomer in a weight percent ratio for a:b ranging from about 1:99 to 99:1 based on the dry weight of said polyampholyte coagulant polymer.

29. A method of producing paper products, the steps comprising:

25 treating coated broke containing white pitch and pigments with a polyampholyte coagulant to attach at least the refines to the fibers of the coated broke;

 adding said coated broke to a paper furnish;

30 prior to a first shearing stage or after the last shearing stage, adding said polyampholyte coagulant to said paper furnish to improve the retention and/or drainage properties of a paper web in producing said paper product.

30. A method for treating process water from a paper mill, the steps comprising:

adding a polyampholyte coagulant to the process water so that the solids in the process water either are floated or settled out; and

removing the solids from the water.

5 31. The method of Claim 30 wherein said polyampholyte coagulant comprises at least two monomers.

32. The method of Claim 30 wherein said polyampholyte coagulant is a copolymer comprising an anionic monomer and a cationic monomer.

10 33. The method of Claim 30 wherein said polyampholyte coagulant r has a weight average molecular weight ranging from about 10 thousand to about 20 million.

34. The method of Claim 30 wherein said polyampholyte coagulant consists of acrylamide (AM), acrylic acid (AA), 15 and dimethyl diallyl ammonium chloride (DADMAC) in a weight percent ratio ranging from about 48:2:50 to about 25:25:50 based on the dry weight of said polyampholyte coagulant.

20 35. The method of Claim 30 wherein said polyampholyte coagulant consists of acrylamide (AM), 2-acrylamido-2-methylpropane sulfonic acid (AMPS), and dimethyl diallyl ammonium chloride (DADMAC) in a weight percent ratio of about 41:13:46.

25 36. The method of Claim 30 wherein said polyampholyte coagulant is present in the paper furnish in an amount of at least 0.0025% by weight based on the dry weight of the solids in the furnish.

30 37. The method of Claim 30 wherein said polyampholyte coagulant comprises a copolymer consisting of (a) an anionic monomer and (b) a cationic monomer in a weight percent ratio for a:b ranging from about 1:99 to 99:1 based on the dry weight of said polyampholyte coagulant.

38. The method of Claim 30 wherein said polyampholyte coagulant comprises at least one anionic monomer selected from the group consisting of acrylic acid, homologues of acrylic acid, sodium acrylate, vinyl sulfonic acid,
5 sodium vinyl sulfonate, itaconic acid, sodium itaconate, 2-acrylamido-2-methylpropane sulfonic acid, sodium salt, acrylamidoglycolic acid, 2-acrylamido-2-methylbutanic acid, 2-acrylamido-2-methylpropanephosphonic acid, sodium vinyl phosphonate, allyl phosphonic acid, and mixtures thereof.
10

39. The method of Claim 38 wherein said polyampholyte coagulant polymer further comprises at least one cationic monomer selected from a group consisting of quaternary dialky dallyl ammonium chloride, methacryloyethyl trimethyl ammonium chloride, quaternized derivatives of dimethyl amino ethyl acrylate, dimethyl amino ethylacrylate, dibutyl aminoethyl methacrylate, dimethyl amino methyl acrylate, demethyl amino methyl methacrylate, diethyl amino propyl methacrylate,
15 acryloyloxethyl trimethyl ammonium methosulfate, amino methylated polyacrylamide, and combinations thereof.
20

40. The method of Claim 39 wherein said anionic and cationic monomers comprise a terpolymer which further comprising at least one nonionic monomer selected from the group of N-vinylamide, N-alkylacrylamide, vinyl acetate, vinyl alcohol, acrylate esters, diacetone acrylamide, N,N-dialkyl- acrylamide.
25

41. The method of Claim 30 wherein said polyampholyte coagulant is a terpolymer consisting of (a) a nonionic monomer, (b) an anionic monomer, and (c) a cationic monomer in a weight percent ratio for a:b:c ranging from about 1:1:98 to about 1:98:1 to about 98:1:1 based on the dry weight of said polyampholyte coagulant polymer.
30

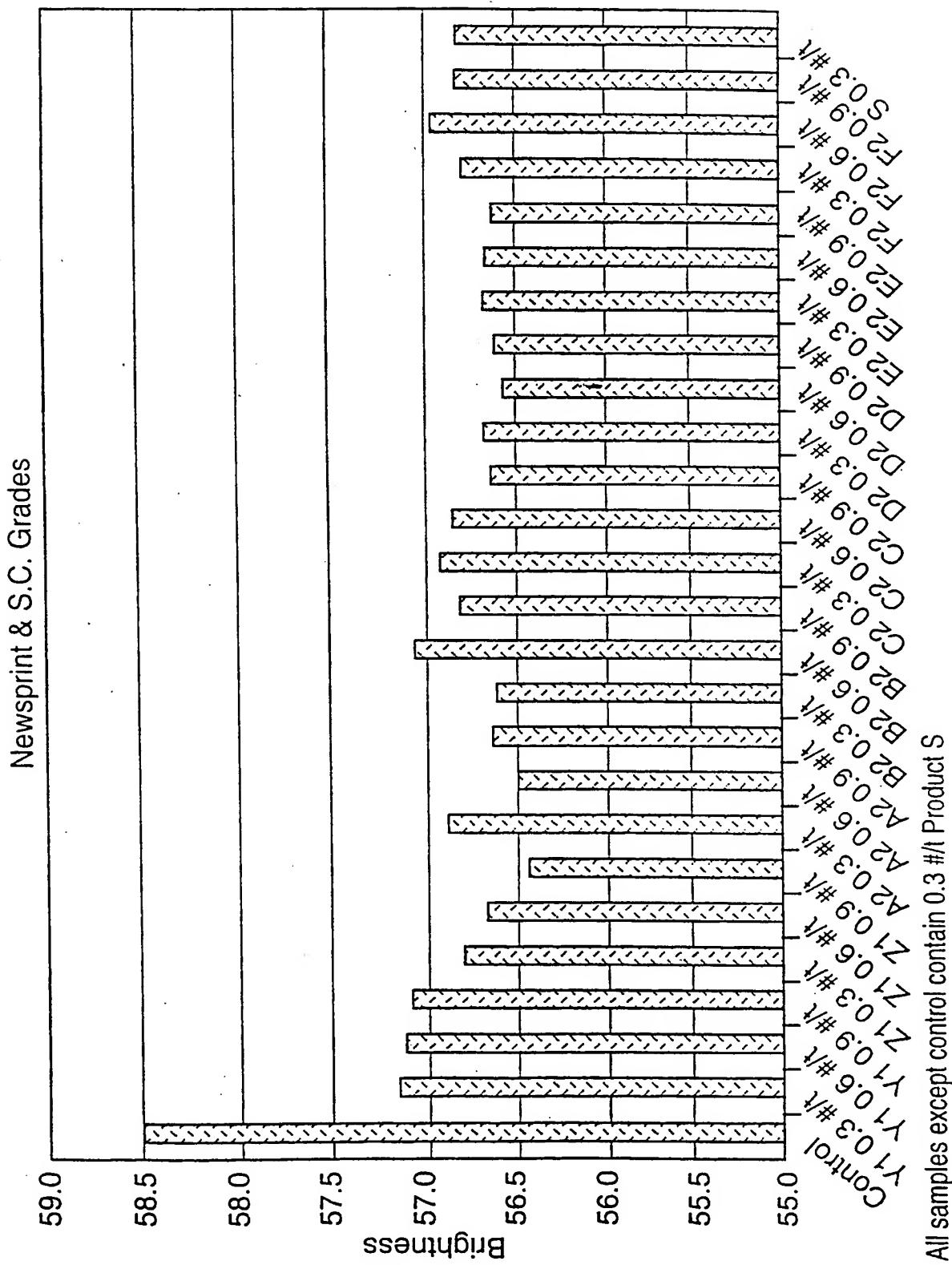
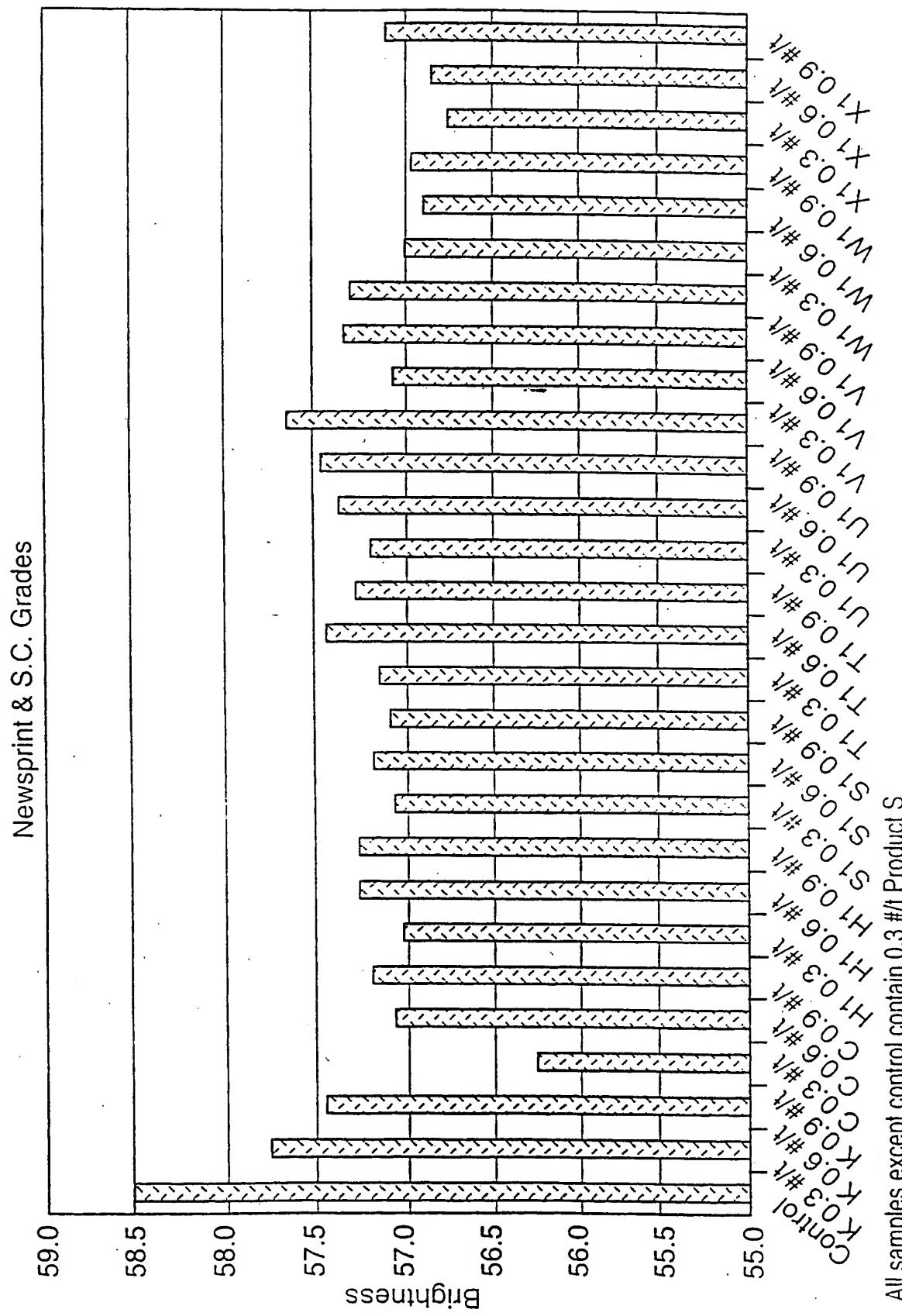


FIG. 4



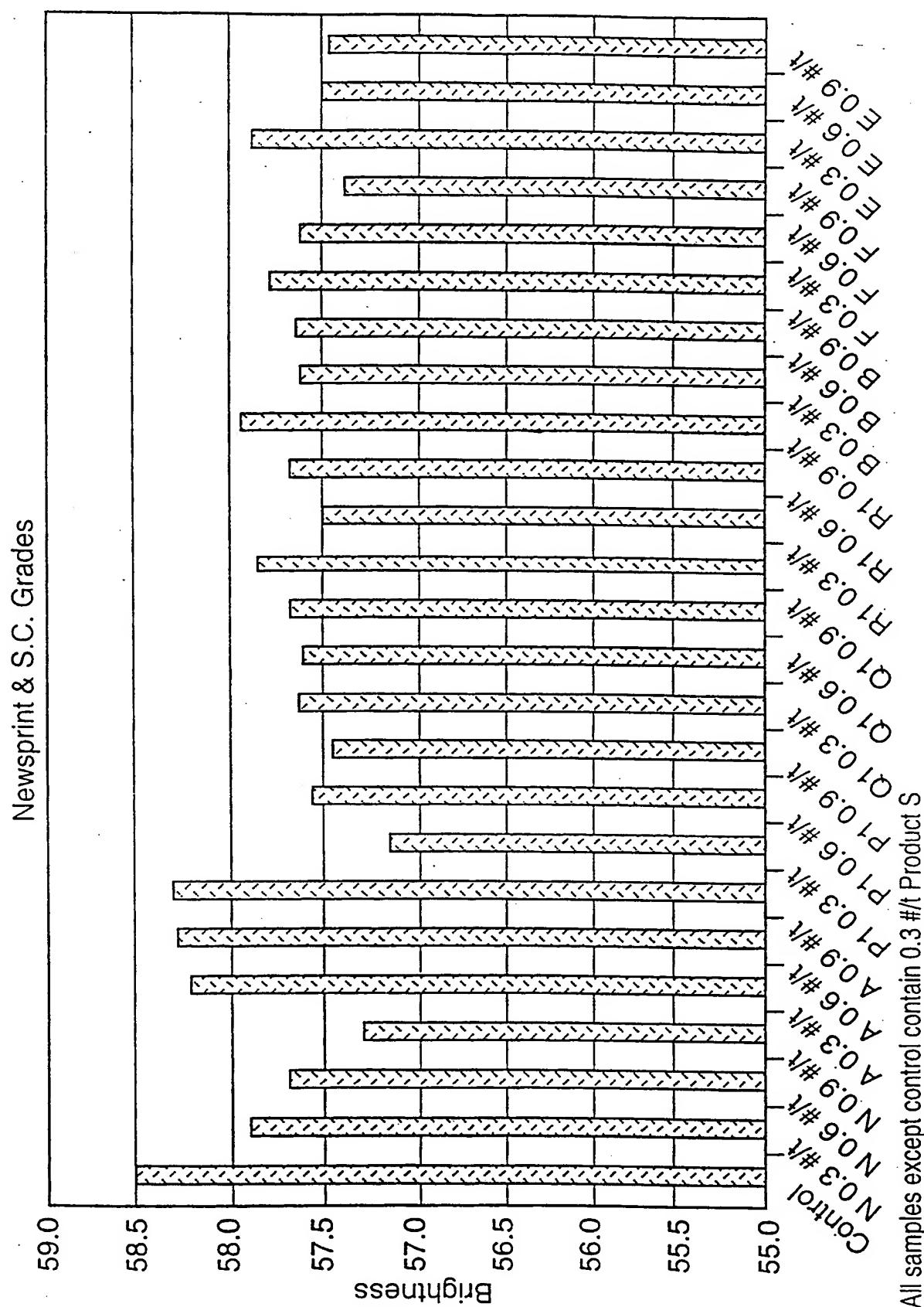
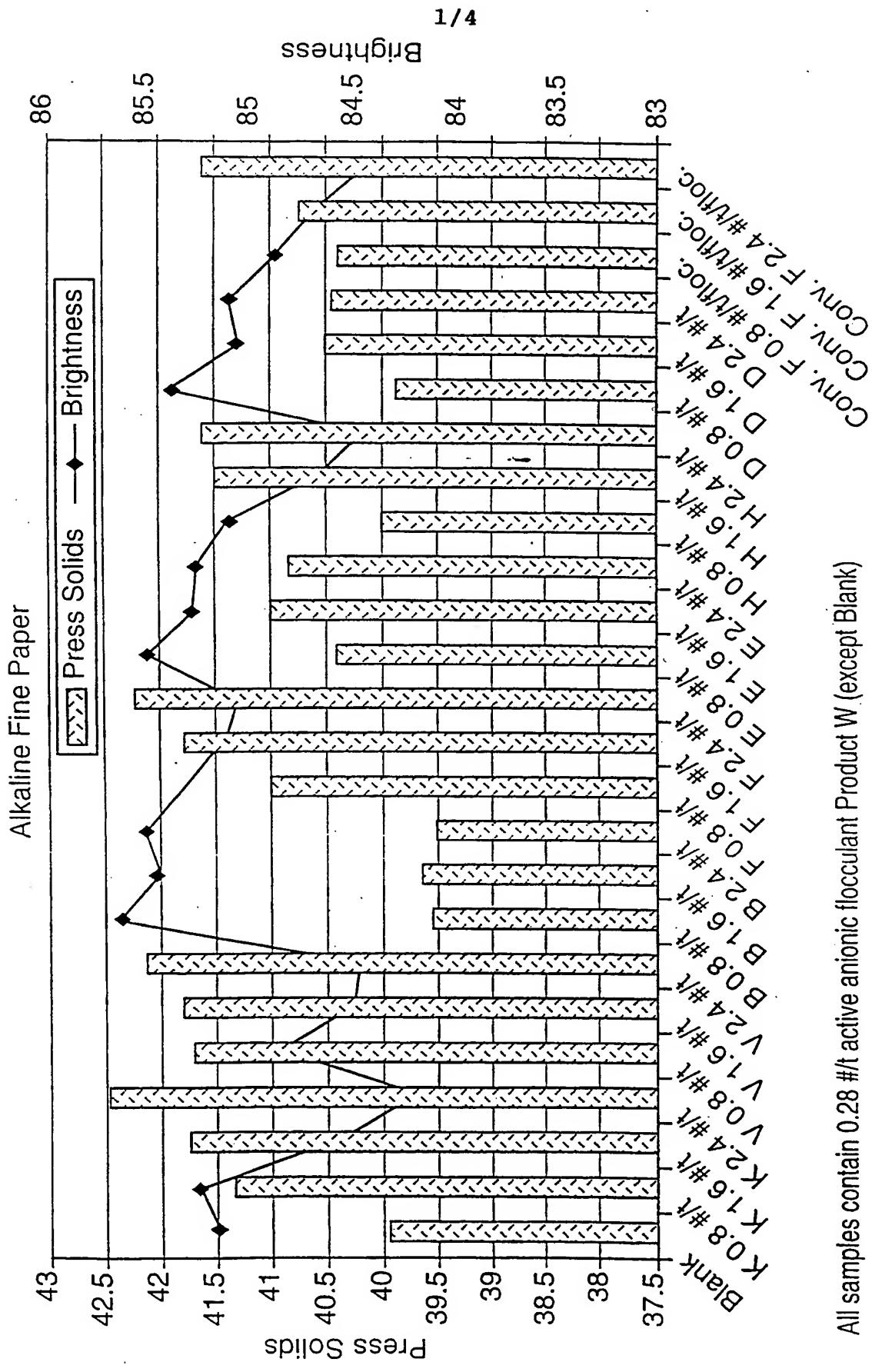


FIG. 2



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/29135

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

The additional search fees were accompanied by the applicant's protest.
 No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/29135

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :D21H 21/10, 17/33, 17/37, 17/41, 17/42, 17/44, 17/45, 17/55
US CL :Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 162/168.3, 168.2, 164.6, 164.1, 166, 167, 168.1, 179, 191, 190, ; 210/928, 705, 723, 702, 704; D21H 21/02.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

East, West, Dialog
search terms: polyampholyte, papermaking, drainage aid, retention aid, coagulant, coated broke.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,505,828 A (LIPOWSKI et al) 19 March 1985, see whole document	1-41
X	US 3,639,208 A (VARVERI et al) 01 February 1972, see entire document.	1-16
Y		17-41
X	EP 0 058 622 A1 (DAIGLE et al) 25 August 1982, see whole document.	1-16
Y		17-41
A	US 5,098,520 A (BEGALA) 24 March 1992, see entire document.	1-41
A	US 3,711,573 A (NAGY) 16 January 1973, see entire document.	1-41

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents:	*T*	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
B earlier document published on or after the international filing date	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A*	document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means		
P document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

09 FEBRUARY 2000

Date of mailing of the international search report

22 FEB 2000

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/29135

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

162/168.3, 168.2, 164.6, 164.1, 166, 167, 168.1, 179, 191; 210/928, 705, 723

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING
This ISA found multiple inventions as follows:

This application contains claims directed to more than one species of the generic invention. These species are deemed to lack Unity of Invention because they are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for more than one species to be searched, the appropriate additional search fees must be paid. The species are as follows:

- I) Composition for use in papermaking slurries.
- II) Composition for treating waste water.

The claims are deemed to correspond to the species listed above in the following manner:

Claims 1-29 correspond to species of group I.
Claims 30-41 correspond to species of group II.

The following claims are generic: None.

The species listed above do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, the species lack the same or corresponding special technical features for the following reasons: The treated systems are not related. The composition is used to treat a papermaking slurry and a waste water which are very different systems.